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27

(Unclassified Title)

**RESEARCH IN HIGH-ENERGY OXIDIZERS**

First Quarterly Report

Fluorine Chemistry Unit  
Chemistry Section  
Research Division

Rocketdyne, a Division of North American Aviation, Inc.  
6633 Canoga Avenue, Canoga Park, California

**TECHNICAL REPORT AFRPL-TR-66-346**

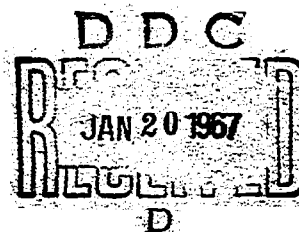
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**RESEARCH IN HIGH-ENERGY OXIDIZERS**

**First Quarterly Report**

**Fluorine Chemistry Unit  
Chemistry Section  
Research Division**

**Rocketdyne, a Division of North American Aviation, Inc.  
6633 Canoga Avenue, Canoga Park, California**

**December 1966**

<p><b>Group 4 Downgraded at 3-Year Intervals Declassified After 12 Years</b></p>
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## FOREWORD

The work reported herein was performed under Contract F04611-67-C-0007 and covers the period 1 September 1966 through 30 November 1966. The program monitor is Lt. Charles Stone (RPCL), Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California.

The project scientist for the program is Dr. D. Filipovich, Principal Scientist of the Fluorine Chemistry Unit. Full-time personnel associated with the program are Dr. W. Maya, Mr. R. D. Wilson, and Mr. M. Warner. The prime program responsibility is in the Synthetic Chemistry Group (Dr. E. A. Lawton, Group Scientist) of the Rocketdyne Research Division.

This report has been assigned the Rocketdyne identification number R-6840-1.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. EBELKE, Colonel, USAF  
Chief, Propellant Division

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## ABSTRACT

The compound  $\text{FCO}_2\text{NF}_2$  is being examined as a potential intermediate for the synthesis of other  $\text{ONF}_2$  compounds. Techniques have been developed for handling  $\text{FCO}_2\text{NF}_2$  to minimize its decomposition to  $\text{F}_2\text{CO}$  and  $\text{FNO}$ ; the pre-treatment of containers with  $\text{BF}_3$  is particularly advantageous in this regard. Compatibility studies of  $\text{FCO}_2\text{NF}_2$  have revealed that it is stable to glass, steel,  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{CO}$ . Water catalyzes the decomposition of the compound and a typical mechanism has been postulated. When  $\text{FCO}_2\text{NF}_2$  undergoes decomposition in the presence of  $\text{C}_2\text{F}_4$ , the latter does not participate in the reaction.

The ultraviolet spectrum of  $\text{FCO}_2\text{NF}_2$  shows an end absorption commencing at 2100 angstroms. Fluorinations of  $\text{FCO}_2\text{NF}_2$ , with and without  $\text{CsF}$ , led only to the production of  $\text{CF}_3\text{OF}$  and nitrogen oxyfluorides. Preliminary experiments to effect condensation reactions of  $\text{FCO}_2\text{NF}_2$  with  $\text{NaNO}_2$  and  $\text{AgNO}_2$  were attempted; only decomposition was observed. A reaction between  $\text{FCO}_2\text{NF}_2$  and sodium trifluoroacetate in trifluoroacetyl anhydride solvent led to the formation of  $\text{CF}_3\text{CFO}$  and  $\text{CF}_3\text{CO}_2\text{NO}$ .

The reaction of  $\text{CF}_3\text{CO}_2\text{NO}$  with  $\text{N}_2\text{F}_4$  in the presence of ultraviolet radiation led to the formation of  $\text{CF}_3\text{NO=NF}$ . With  $\text{ClNF}_2$ ,  $\text{CF}_3\text{CO}_2\text{NO}$  gave  $\text{CF}_3\text{CFO}$ ,  $\text{NOCl}$ , and  $\text{N}_2\text{F}_4$  as the principal products, which are shown to have arisen probably via the formation of  $\text{CF}_3\text{CO}_2\text{NF}_2$ .

The photolysis of mixtures of trifluoroacetyl anhydride and  $\text{N}_2\text{F}_4$  resulted in the formation of  $\text{CF}_3\text{NF}_2$ .

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The synthesis of tetrafluorourea from perfluoroformamide and KF has been examined, and this reaction involves a labile  $\text{NF}_2$  group of potential utility as a new synthetic tool. The interaction of trifluoroacetyl anhydride with the KF complex of perfluoroformamide led to the formation of  $\text{CF}_3\text{CONF}_2$ . The nature of the complex between KF and excess perfluoroformamide was examined, and it has been demonstrated that after aging at  $-40^\circ\text{C}$  the complex present is probably that of tetrafluorourea and KF.

(Confidential Abstract)



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## INTRODUCTION

This is the first quarterly report on a research program designed to exploit the use of the  $\text{ONF}_2$  oxidizing group in high-energy oxidizer candidates. Previous work under other contracts, had resulted in the preparation of  $\text{CF}_2(\text{ONF}_2)_2$  (Ref. 1) and  $\text{FOCF}_2\text{ONF}_2$  (Ref. 2). In addition, it had been shown that, with  $\text{CF}_2(\text{ONF}_2)_2$ , no sensitivity problem existed (Ref. 2) and this stability was expected to be conferred on higher homologs. Thus, the principal aim of this present program is to seek methane derivatives with three or four  $\text{ONF}_2$  oxidizing groups.

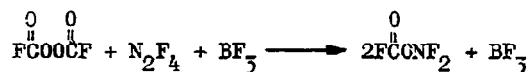
Effort during the first quarter was concentrated on a study of the use of perfluoroacyl nitrites as model compound intermediates in the formation of acyl  $\text{ONF}_2$  derivatives. In addition to describing the results in this area, this report also covers in detail the initiation of a concentrated study of the chemistry of difluoroaminoxycarbonyl fluoride and perfluoroformamide. The potential of both of these intermediates will be discussed in detail with respect to their utility in preparing more energetic oxidizers.

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## DISCUSSION

### THE CHEMISTRY OF DIFLUOROAMINOXY CARBONYL FLUORIDE, $\text{FCO}_2\text{NF}_2$

Difluoroaminoxy carbonyl fluoride is a potential intermediate for the synthesis of  $\text{ONF}_2$  compounds provided the fluorocarbonyl group can be utilized synthetically without cleaving the  $\text{ONF}_2$  group. This compound has been synthesized (Ref. 2), by the reaction of bis-(fluorocarbonyl) peroxide (Ref. 3) and  $\text{N}_2\text{F}_4$  in the presence of a small amount of  $\text{BF}_3$ :



Although the  $\text{BF}_3$  does not enter into the reaction, it presumably acts as a stabilizer for  $\text{FCO}_2\text{NF}_2$ ; this latter compound has been found to decompose rapidly according to the following equation:



The presence of  $\text{BF}_3$  does not prevent this decomposition from taking place, but it has been found to lessen the frequency. Infrequently, pure  $\text{FCO}_2\text{NF}_2$  has been found to be stable in glass for long periods of time. However, once the  $\text{FCO}_2\text{NF}_2$  starts to decompose, either pure or in mixtures with  $\text{BF}_3$ , the decomposition cannot be arrested and is complete in a matter of minutes. The instability of  $\text{FCO}_2\text{NF}_2$  has been a barrier to the facile development of the chemistry of  $\text{FCO}_2\text{NF}_2$ . The compound has been, at times, so unstable that little more than its infrared spectrum could be determined before decomposition began. Thus, to utilize this compound, its handling aspects have been studied in detail and have progressed to the point where meaningful studies can be initiated.

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## Compatibility Studies

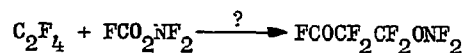
Mixtures of  $\text{FCO}_2\text{NF}_2$  containing 10-percent  $\text{BF}_3$  have limited stability in glass and in stainless steel. Traces of water are enough to cause the decomposition of a large amount of  $\text{FCO}_2\text{NF}_2$ . A small amount of water vapor was admitted into an infrared cell containing  $\text{FCO}_2\text{NF}_2$  and  $\text{BF}_3$ . The spectrum, taken immediately afterward, showed only the disappearance of the  $\text{BF}_3$ . On admitting a further small amount of water vapor, the  $\text{FCO}_2\text{NF}_2$  decomposed immediately before the spectrum could be recorded. Decomposition of  $\text{FCO}_2\text{NF}_2$  has been observed with sodium fluoride but this experiment did not determine whether the sodium fluoride initiated the decomposition or merely caused it by removal of the  $\text{BF}_3$ .

## Ultraviolet Spectrum of $\text{FCO}_2\text{NF}_2$

The ultraviolet spectrum of  $\text{FCO}_2\text{NF}_2$ , containing 10-percent  $\text{BF}_3$ , was taken to ascertain whether this compound is suited to photochemical reactions. The spectrum of the gas at 400 millimeters showed only an end absorption at 2100 angstroms; it is therefore concluded that light does not initiate the facile decomposition of  $\text{FCO}_2\text{NF}_2$ .

## Mechanism of Decomposition

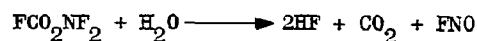
Difluoroaminoxycarbonyl fluoride has been found to be unreactive with  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{C}_2\text{F}_4$ . With  $\text{C}_2\text{F}_4$ , the possibility existed that decomposition intermediates of  $\text{FCO}_2\text{NF}_2$  might have added to the olefin:



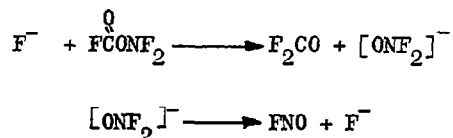
However, the  $\text{FCO}_2\text{NF}_2$  was found to decompose in the presence of  $\text{C}_2\text{F}_4$  without affecting the latter. This result, together with the unreactivity of  $\text{FCO}_2\text{NF}_2$  towards  $\text{NO}$  and  $\text{O}_2$ , indicates there is no chain radical mechanism for the decomposition of  $\text{FCO}_2\text{NF}_2$ . Otherwise, it would be expected that  $\text{O}_2$  or  $\text{NO}$  would have catalyzed the decomposition, or that  $\text{CO}$  or  $\text{C}_2\text{F}_4$  would have acted as radical traps.

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A mechanism for the decomposition of  $\text{FCO}_2\text{NF}_2$  is not immediately apparent but probably includes a base catalysis step. Water would hydrolyze the acyl halide but a propagation step is not readily obvious:



A specific base catalyzed reaction may involve the  $\text{F}^-$  as follows:



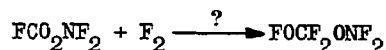
Here, both initiation and propagation steps are immediately obvious.

### Handling Method

In an attempt to rigorously exclude moisture, bases, and active hydrogen sources from coming into contact with  $\text{FCO}_2\text{NF}_2$ , all apparatus used was pretreated with  $\text{BF}_3$ . This practice has been effective, and it is now possible to handle  $\text{FCO}_2\text{NF}_2$  containing 10-percent  $\text{BF}_3$  for extended periods without decomposition.

### Fluorination of $\text{FCO}_2\text{NF}_2$

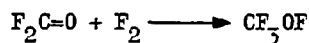
The fluorination of  $\text{FCO}_2\text{NF}_2$  was undertaken to determine whether the known compound  $\text{FOCF}_2\text{ONF}_2$  (Ref. 2) could be synthesized in this manner:



A total of 10 fluorinations were performed and are summarized in the experimental section of this report. Under a variety of conditions, the only products found were  $\text{CF}_3\text{OF}$  and nitrogen oxides and oxyfluorides.

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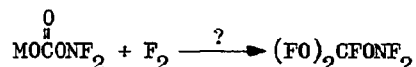
However, it is not clear at this time whether the  $\text{CF}_3\text{OF}$  formed is a primary product, or whether it results from the fluorination of the decomposition product of  $\text{FCO}_2\text{NF}_2$ , i.e.,  $\text{COF}_2$ :



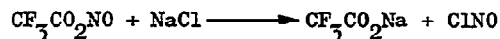
This question probably will be resolved during future work at Rocketdyne as more experience and knowledge is gained concerning the properties of  $\text{FCO}_2\text{NF}_2$ .

## Condensation Reactions

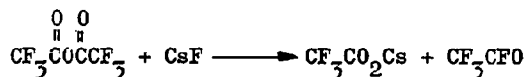
A promising possibility is the formation of a salt,  $\text{MO}_2\text{CONF}_2$  (where M is a metal) from  $\text{FCO}_2\text{NF}_2$ . Such a salt could lead to trifunctional fluoromethanes:



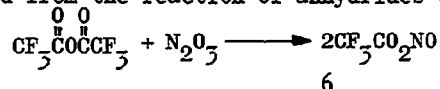
Because  $\text{FCO}_2\text{NF}_2$  is unstable in the presence of compounds containing an active hydrogen, indirect approaches to the formation of the salts have been undertaken. One approach involved the projected synthesis of an acyl nitrite,  $\text{F}_2\text{NOCO}_2\text{NO}$ , from  $\text{FCO}_2\text{NF}_2$ . Acyl nitrites are known to undergo reaction with metal halides to give the corresponding carboxy salts (Ref. 4):



Another approach consists in the synthesis of a mixed anhydride from  $\text{FCO}_2\text{NF}_2$ , such as  $\text{CF}_3\text{CO}_2\text{CO}_2\text{NF}_2$ . Anhydrides can lead to salts either by reaction with salts (Ref. 5):



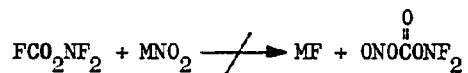
or by the intermediate formation of acyl nitrites, which are formed in high yield from the reaction of anhydrides with  $\text{N}_2\text{O}_3$  (Ref. 6):



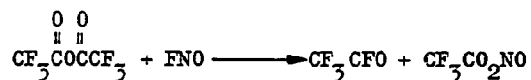
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Both approaches have been examined cursorily during this period. The reactions of  $\text{FCO}_2\text{NF}_2$  with  $\text{NaNO}_2$  and  $\text{AgNO}_2$  were attempted:



With both salts, the  $\text{FCO}_2\text{NF}_2$  quickly decomposed to  $\text{F}_2\text{CO}$  and  $\text{FNO}$ . A more suitable reaction environment will be provided through the use of solvents. Accordingly, a search for solvents for  $\text{FCO}_2\text{NF}_2$  was initiated. The first successful candidate is trifluoroacetic anhydride inasmuch as  $\text{FCO}_2\text{NF}_2$  was recovered from it after 45 minutes at room temperature with a minimum of decomposition. The synthesis of a mixed anhydride was attempted by the reaction of  $\text{FCO}_2\text{NF}_2$  with sodium trifluoroacetate in trifluoroacetic anhydride as the solvent. The principal products of the reaction were  $\text{CF}_3\text{CFO}$  and  $\text{CF}_3\text{CO}_2\text{NO}$ ; both products are thought to arise by the interaction of trifluoroacetic anhydride with  $\text{FNO}$  formed during the reaction:



The presence of any moisture or free acid in the anhydride would make a fluoride ion available to the system, and fluoride ions, as discussed previously, may catalyze the decomposition of  $\text{FCO}_2\text{NF}_2$  to form  $\text{FNO}$ . Future work will entail the use of other solvents, and emphasis will be placed on ensuring the removal of all traces of substances containing active hydrogen from the system.

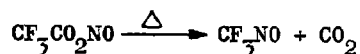
### REACTIONS OF TRIFLUOROACETYL DERIVATIVES

The reactions of trifluoroacetyl compounds with  $\text{N}_2\text{F}_4$  have been studied as models (Ref. 3) for possible routes to the synthesis of homologs of  $\text{FCO}_2\text{NF}_2$  compounds.

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## Reactions of Trifluoroacetyl Nitrite

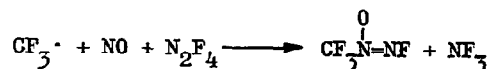
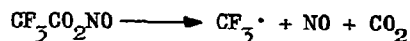
Trifluoroacetyl nitrite was selected for this study because of its well-known thermal dissociation (Ref. 7):



This indicated that the intermediate  $\text{CF}_3\text{CO}_2\cdot$  radical may exist briefly during the dissociation. With  $\text{N}_2\text{F}_4$  present during this process, the formation of  $\text{CF}_3\text{CO}_2\text{NF}_2$  becomes a distinct possibility.

Thermal reactions between  $\text{CF}_3\text{CO}_2\text{NO}$  and  $\text{N}_2\text{F}_4$ , run in static systems at 70 C and in flow systems at 180 C, led to complete recovery of the starting materials.

Thermal reactions were abandoned in favor of ultraviolet excitation. The photolysis of  $\text{CF}_3\text{CO}_2\text{NO}$  led to the formation of  $\text{CF}_3\text{NO}$  and  $\text{CO}_2$ , completely analogous to the thermal process. Concurrent with this work, a study of the photolysis of  $\text{CF}_3\text{CO}_2\text{NO}$  appeared in Ref. 8 which presented essentially the same results. When mixtures of  $\text{CF}_3\text{CO}_2\text{NO}$ ,  $\text{N}_2\text{F}_4$ , and  $\text{BF}_3$  (to stabilize any  $\text{CF}_3\text{CO}_2\text{NF}_2$  formed) were photolyzed, the main product was  $\text{CF}_3\text{NO}=\text{NF}$ , which is known to arise whenever  $\text{NO}$ ,  $\text{N}_2\text{F}_4$ , and  $\text{CF}_3\cdot$  radicals are present (Ref. 5 and 9):

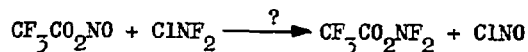


These results indicate that the decomposition of the radical  $\text{CF}_3\text{CO}_2\cdot$  to the  $\text{CF}_3\cdot$  radical and  $\text{CO}_2$  is fast enough to preclude the formation of  $\text{CF}_3\text{CO}_2\text{NF}_2$ , at least under the experimental conditions used. No further work is contemplated on this approach at this time.

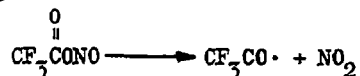


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The reaction of  $\text{CF}_3\text{CO}_2\text{NO}$  with  $\text{ClNF}_2$  was also considered as a route to  $\text{CF}_3\text{CO}_2\text{NF}_2$ :



The reaction was carried out at room temperature for 20 hours; in addition to starting materials, products obtained were  $\text{NOCl}$ ,  $\text{CF}_3\text{CFO}$ ,  $\text{N}_2\text{F}_4$ ,  $\text{NO}_2$ , a trace of  $\text{SiF}_4$ , and probably  $\text{Cl}_2$ , identified tentatively by its color and volatility. The formation of these products can be accounted for easily if the transitory formation of  $\text{CF}_3\text{CO}_2\text{NF}_2$  is postulated with its facile decomposition to  $\text{CF}_3\text{CFO}$  and  $\text{FNO}$  (analogous to the behavior of  $\text{FCO}_2\text{NF}_2$ ). The presence of  $\text{FNO}$  probably would not be detected under these conditions, because it would, by attacking the glass, be present as  $(\text{NO})_2\text{SiF}_6$ . Other routes to the formation of  $\text{CF}_3\text{CFO}$  are not immediately apparent, because  $\text{CF}_3\text{CO}_2\text{NO}$  is known to cleave easily to give  $\text{NO}$ , but not  $\text{NO}_2$ . The formation of  $\text{CF}_3\text{CFO}$  would imply the unlikely cleavage:

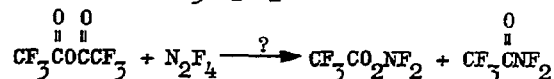


Ionic attack of fluorides on the nitrite also would not lead to the formation of  $\text{CF}_3\text{CFO}$ , but to the formation of acetate salts (Ref. 4):



### Reaction of Trifluoroacetic Anhydride

The photolysis of mixtures of trifluoroacetic anhydride and  $\text{N}_2\text{F}_4$  were examined as a route to  $\text{CF}_3\text{CO}_2\text{NF}_2$ :



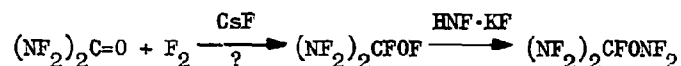
The result of a first attempt was the formation of  $\text{CF}_3\text{NF}_2$ ,  $\text{CO}_2$ , and a carbonyl compound, probably  $\text{CF}_3\text{CFO}$ . The  $\text{CF}_3\text{NF}_2$  was identified by its infrared spectrum (Ref. 10). This reaction constitutes a novel synthesis of  $\text{CF}_3\text{NF}_2$ , and although an exhaustive literature search has not been made,

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appears to constitute the first instance of a photochemical reaction of trifluoroacetic anhydride. The formation of  $\text{CF}_3\text{NF}_2$  implies that the radical  $\text{CF}_3\text{CO}_2\cdot$  was formed, but that it is too unstable to react with  $\text{N}_2\text{F}_4$  prior to decomposition.

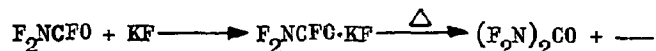
### CHEMISTRY OF PERFLUOROFORMAMIDE

The chemistry of perfluoroformamide leading to  $(\text{NF}_2)_2\text{CO}$ , reported by Frazer and Shraeve (Ref. 11) offers a number of possibilities for exploitation. The tetrafluorourea itself is of interest as an intermediate in the synthesis of a novel oxidizer containing both  $\text{NF}_2$  and  $\text{ONF}_2$  groups:



The resulting compound could be examined for any attenuating effect of the  $\text{ONF}_2$  group on the sensitivity of the  $\text{C}(\text{NF}_2)_2$  group.

An understanding of the chemistry and the techniques of the tetrafluorourea synthesis which could be extended to other systems aimed at the synthesis of new  $\text{CONF}_2$  compounds is of immediate interest. The synthesis reported by Frazer and Shreeve seems to consist of two steps: (1) formation of a difluoroaminocarbonyl fluoride-KF complex, and (2) pyrolysis of the complex:



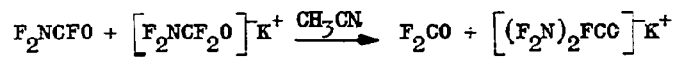
An interesting aspect of these reactions is the implied migration of an  $\text{NF}_2$  group from one carbon atom to another, either by a concerted or step-wise mechanism, which could be of wide synthetic utility.

An initial attempt to repeat this work resulted in an explosive decomposition of the complex during pyrolysis, an anticipated event which affirmed that proper techniques were used in the complexing step. The complexing step was then studied in greater detail, resulting in the following facts.

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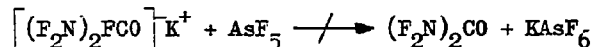
1. Complexing of  $F_2NCF_2O$  and  $KF$  does not take place in a heterogeneous system, but does take place in a rigorously anhydrous acetonitrile solvent.
2. Success of the synthesis of the complex depends on the use of excess  $F_2NCF_2O$ , ideally 2 moles of  $F_2NCF_2O$  per mole of  $KF$ , and allowing sufficient time (1 or more days) for the complexing step at  $-40\text{ C}$  in acetonitrile.
3. The complexing step is accompanied by the evolution of  $F_2CO$  corresponding to approximately one-half of the total amount of  $F_2NCF_2O$ .

Thus, the solid complex obtained after removal of volatile material may be of the composition indicated in the following equation:

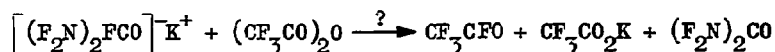


Smooth decomposition of the underlined complex should give tetrafluorourea and  $KF$ .

An attempt was made to displace tetrafluorourea from the complex with  $AsF_5$ :



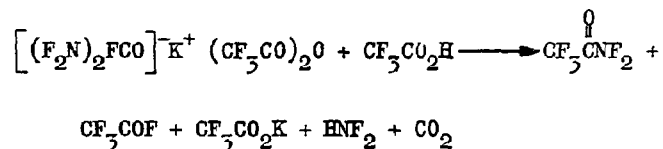
However, there was no reaction upon contact of gaseous or liquid  $AsF_5$  with the complex, demonstrating the reduced reactivity of the complex in the absence of a solvent. The complex was treated with trifluoroacetic anhydride in an attempt to effect the displacement:



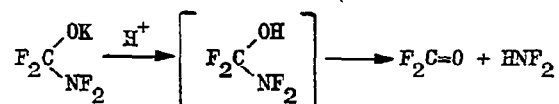
The major volatile products obtained from the reaction consisted of  $CF_3CONF_2$  and  $CF_3CFO$ , the combined amounts of which nearly corresponded to the initial amount of  $F_2NCF_2O$  used. Also obtained were smaller amounts of  $HNF_2$ ,  $CO_2$ , and  $CF_3CO_2H$  indicative of moisture contamination. No perfluorourea was found. Although the presence of moisture complicated the results, the formation of  $CF_3CONF_2$  suggests a  $NF_2^-$  anion transfer from

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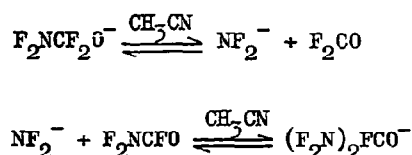
what was probably the perfluorourea and KF complex. The following equation depicts the apparent course of reaction between the complex of tetrafluorourea and KF and trifluoroacetic anhydride contaminated with moisture:



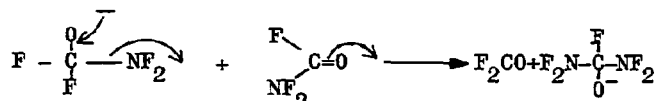
The formation of  $\text{HNF}_2$  is the expected consequence of the action of a proton displacing the metal ion from the complex, and subsequent elimination of  $\text{HNF}_2$ :



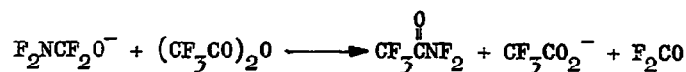
The observed transfer of  $\text{NF}_2^{-}$  anion in the trifluoroacetic anhydride reaction helps substantiate the contention that a very similar process occurred in the synthesis of perfluorourea itself, which may be more simply depicted by two equilibria involving solvated species:



or the process can be visualized as a concerted displacement:



Significant, also, is the observation that  $\text{CO}_2$  and not  $\text{F}_2\text{CO}$  was produced in the trifluoroacetic anhydride reaction, indicating that the reactive species could not have been  $(\text{F}_2\text{NCF}_2\text{O})^{-}\text{K}^{+}$ , which would have produced  $\text{F}_2\text{CO}$ :



At least some  $\text{F}_2\text{CO}$ , if produced, should have survived even the moisture-contaminated trifluoroacetic anhydride.

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Future plans include direct fluorinations of the perfluorourea and KF complex, further exploration of the  $\text{NF}_3$  transfer phenomenon, and extension of the perfluorourea synthesis techniques to other systems.

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## EXPERIMENTAL

### CHEMISTRY OF $\text{FCO}_2\text{NF}_2$

#### Preparation of $\text{F}_2\text{C}_2\text{O}_4$

Bis-(fluorocarbonyl) peroxide was prepared by the action of fluorine on CO and  $\text{O}_2$  (Ref. 3).

#### Preparation of $\text{FCO}_2\text{NF}_2$

A 300-milliliter Pyrex ampoule fitted with either a high-vacuum stopcock or a Fisher-Porter valve was flamed out and pretreated with approximately 400 millimeters of  $\text{BF}_3$ . The ampoule was loaded by condensation with  $\text{F}_2\text{C}_2\text{O}_4$  (50 cc),  $\text{N}_2\text{F}_4$  (50 cc), and approximately 10 cc of  $\text{BF}_3$ . The ampoule was stored at room temperature for 2 days; at the end of this period the infrared spectrum of the material revealed almost complete reaction to  $\text{FCO}_2\text{NF}_2$ , and the  $\text{BF}_3$  was still present. Arsenic pentafluoride was also employed in the place of  $\text{BF}_3$ , but did not offer any advantage. The yields of  $\text{FCO}_2\text{NF}_2$  were of the order of 80 percent.

#### Fluorination of $\text{FCO}_2\text{NF}_2$

The fluorinations were conducted in Type 304 stainless-steel Hoke cylinders fitted with stainless-steel valves, that had been passivated with fluorine for a minimum of 12 hours. The fluorinations are listed in Table 1. In a typical preparation, the  $\text{FCO}_2\text{NF}_2$  it employed was loaded in a dry box. The  $\text{FCO}_2\text{NF}_2$  (30 to 40 cc) was condensed into the cylinder and an appropriate amount of fluorine was condensed in at  $-196^\circ\text{C}$ . The cylinder was placed in a bath made from a slurry of Dry Ice powder and liquid nitrogen, and allowed to warm gradually to  $-80^\circ\text{C}$ . After the specified reaction time, the fluorine was pumped off at  $-196^\circ\text{C}$ , and the remainder of the reaction mixture was worked up in the usual manner in a glass high-vacuum line.

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TABLE 1

FLUORINATION OF  $\text{FCONF}_2^*$

Fluorination No.	Cylinder volume, milliliters	Fluoride Used of $\text{CaF}_2$	Approximate Volume of Fluorine	Reaction Temperature, $^{\circ}\text{C}$	Reaction Time	Products
1	30	5 grams of $\text{CaF}_2$	1 liter	-80	3 days	$\text{CF}_3\text{OF}$ , $\text{NO}_2$ , $\text{NOF}$ , $\text{FNO}_2$
2			1 liter		4 days	$\text{CF}_3\text{OF}$ , $\text{NO}_2$ , $\text{NOF}$ , $\text{FNO}_2$
3			No fluorine (control experiment)		~16 hours	Recovered unreacted $\text{FCONF}_2$ , $\text{COF}_2$ , $\text{FNO}$ , $\text{FNO}_2$
4			1 liter		~16 hours	$\text{CF}_3\text{OF}$ , $\text{NO}_2$
5		5 grams of $\text{CaF}_2$			2 days	$\text{CF}_3\text{OF}$ , $\text{NO}_2$
6		5 grams of $\text{CaF}_2$	100 cc		~16 hours	Unreacted $\text{FCOOCF}$ and $\text{N}_2\text{F}_4$ , $\text{CF}_3\text{OF}$ , $\text{NO}_2$ , trace of unknown
7			100 cc		~16 hours	The $\text{FCONF}_2$ was recovered and reused
8**			500 cc		3 days	$\text{CF}_3\text{OF}$ , $\text{NO}_2$ , trace of $\text{FCOOCF}$
9			500 cc		5 days	$\text{COF}_2$ , $\text{FNO}$ , $\text{NO}_2$ , trace of $\text{FCOOCF}$ , $\text{BF}_3$ , trace of unknown
10		5 grams of $\text{CaF}_2$	500 cc		6 days	$\text{CF}_3\text{OF}$ , $\text{NOF}$ , $\text{N}_2\text{F}_4$ , $\text{COF}_2$ , trace of $\text{FCOOCF}$ , trace of unknown

\*Reactant  $\text{FCONF}_2$  was used directly from preparation, and in some cases contained unreacted  $\text{FCOOCF}$ ,  $\text{N}_2\text{F}_4$ , and  $\text{BF}_3$ .

\*\*Reused  $\text{FCONF}_2$  from reaction 7

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## REACTIONS OF TRIFLUOROACETYL DERIVATIVES

### Synthesis of $\text{CF}_3\text{CO}_2\text{NO}$

Trifluoroacetyl nitrite was synthesized by the reaction of  $\text{N}_2\text{O}_5$  and the anhydride (Ref. 6).

### Photolysis Reactions

The photolysis reactions were conducted in Vycor and quartz vessels, and the irradiations were performed at room temperature with a Hanovia Utility Lamp, Type 30620, rated at 140 watts. The products were analyzed by infrared spectroscopy after trap-to-trap distillation in a high-vacuum line.

## CHEMISTRY OF PERFLUOROFORMAMIDE

### Preparation

The ultraviolet-initiated reaction of CO and  $\text{N}_2\text{F}_4$  was carried out as reported by Frazer and Shreeve (Ref. 12) except that higher yields were obtained (25 to 30 percent) through the use of an air-cooled, low-pressure mercury vapor Hanovia Utility Lamp, Type 30620, and an ice water-cooled 2-liter reactor flask.

### Preparation of Activated Potassium Fluoride

A special apparatus was fabricated for the purpose of depositing a measured amount of activated KF in a reaction flask. The operation consisted of passing gaseous hexafluoroacetone (HFA) into a suspension of fusion-dried KF in anhydrous acetonitrile at  $-30^\circ\text{C}$ . The resulting solution of the KF·HFA complex in acetonitrile was forced through a sintered glass filter



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and into the reactor. The solvent was then pumped off and the complex decomposed by warming it to 100 C, leaving an amount of activated KF which closely corresponds to the quantity of hexafluoroacetone used. One mmole of hexafluoroacetone measured by flowmeters delivers approximately 0.87 mmole of KF.

### Complex Formation

Into a 200-milliliter Pyrex reactor containing activated KF (1.1 mmoles) was condensed  $F_2NCF_3$  (50 cc) and anhydrous acetonitrile (approximately 3 milliliters). The mixture was stored at -40 C for several days. Removal of volatile material at 0 C and fractionating through -80, -142, and -196 C traps gave  $CF_3O$  (approximately 25 cc) and  $CH_3CN$ . No  $F_2NCF_3$  was detected by infrared analyses. The white solid remaining in the reactor is believed to be the tetrafluorourea KF complex.

### Attempted Displacement of TFU with $AsF_5$

To the previously described complex was added  $AsF_5$  (50 cc) at -196 C. The mixture was warmed to room temperature and refrozen several times. The  $AsF_5$  was recovered quantitatively. The ampoule was then reloaded with  $AsF_5$  (350 cc) and thermostatted at -65 C for 4 hours. Again, the  $AsF_5$  was recovered without reaction.

### Reaction of TFU-KF Complex With $(CF_3CO)_2O$

To the ampoule containing the TFU-KF complex was added  $(CF_3CO)_2O$  (215 cc) and the mixture was maintained at 0 C overnight. Fractionation and infrared analysis of the volatile products revealed  $CF_3CONF_2$  (22 cc),  $CF_3COF$  (22 cc),  $HNF_2$  (5 cc),  $CO_2$  (6 cc), and unreacted  $(CF_3CO)_2O$ . The solid residue was heated to 100 C with pumping only to yield a small amount of  $CF_3COOH$  indicating moisture contamination of the reaction.

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13. ABSTRACT The compound $\text{FCO}_2\text{NF}_2$ is being examined as a potential intermediate for the synthesis of other $\text{ONF}_2$ compounds. Compatibility studies of $\text{FCO}_2\text{NF}$ have revealed that it is stable to glass, steel, $\text{NO}$ , $\text{O}_2$ , and $\text{CO}$ . Water catalyzes the decomposition of the compound and a typical mechanism has been postulated. When $\text{FCO}_2\text{NF}_2$ undergoes decomposition in the presence of $\text{C}_2\text{F}_4$ , the latter does not participate in the reaction. Fluorinations of $\text{FCO}_2\text{NF}_2$ , with and without $\text{CsF}$ , led only to the production of $\text{CF}_3\text{OF}$ and nitrogen oxyfluorides. Preliminary experiments to effect condensation reactions of $\text{FCO}_2\text{NF}_2$ with $\text{NaNO}_2$ and $\text{AgNO}_2$ were attempted; only decomposition was observed. The reaction of $\text{CF}_3\text{CO}_2\text{NO}$ with $\text{N}_2\text{F}_4$ in the presence of ultraviolet radiation led to the formation of $\text{CF}_3\text{NO-NF}$ . With $\text{ClNF}_2$ , $\text{CF}_3\text{CO}_2\text{NO}$ gave $\text{CF}_3\text{CFO}$ , $\text{NOCl}$ , and $\text{N}_2\text{F}_4$ as the principal products, which are shown to have arisen probably via the formation of $\text{CF}_3\text{CO}_2\text{NF}_2$ . The photolysis of mixtures of trifluoroacetyl anhydride and $\text{N}_2\text{F}_4$ resulted in the formation of $\text{CF}_3\text{NF}_2$ . The synthesis of tetrafluorourea from perfluoroformamide and $\text{KF}$ has been examined, and this reaction involves a labile $\text{NF}_2$ group of potential utility as a new synthetic tool. The interaction of trifluoroacetyl anhydride with the $\text{KF}$ complex of perfluoroformamide led to the formation of $\text{CF}_3\text{CONF}_2$ . The nature of the complex between $\text{KF}$ and excess perfluoroformamide was examined, and it has been demonstrated that after aging at $-40^\circ\text{C}$ the complex present is probably that of tetrafluorourea and $\text{KF}$ . (C)		

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14. KEY WORDS	LINK A		LINK B		LINK C	
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